

Combustion Chemistry at High Pressure: A Perspective from Theory and Modeling

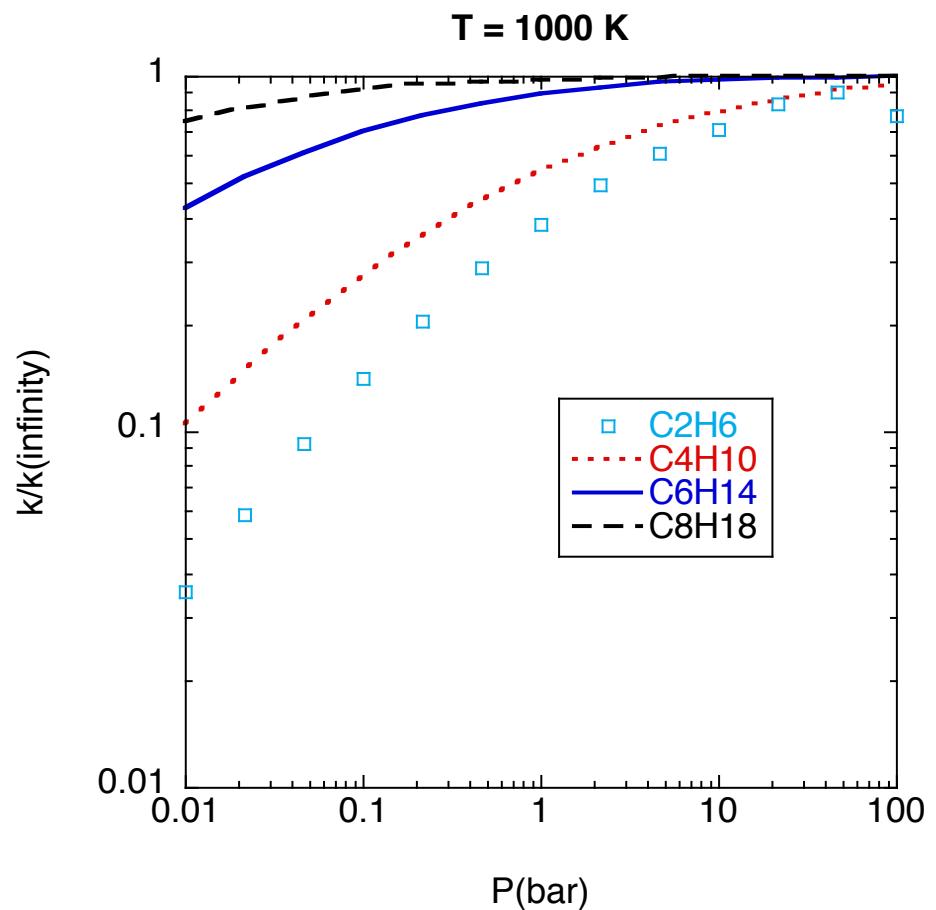
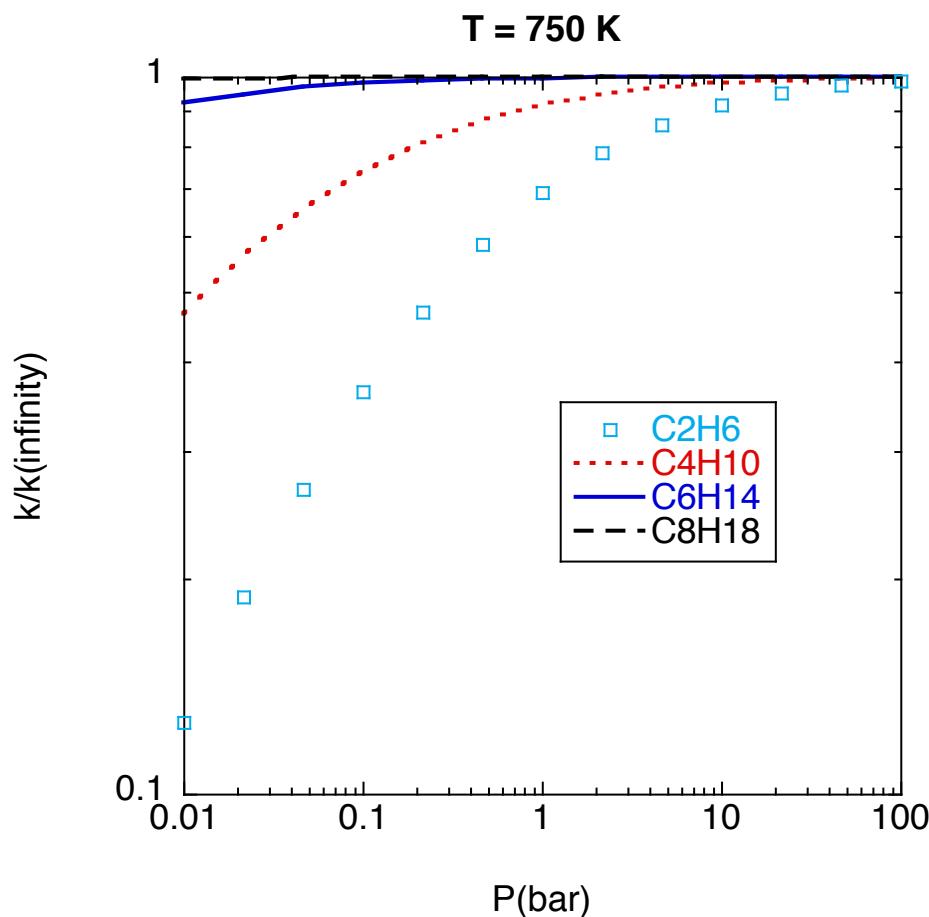
Stephen J. Klippenstein

Outline

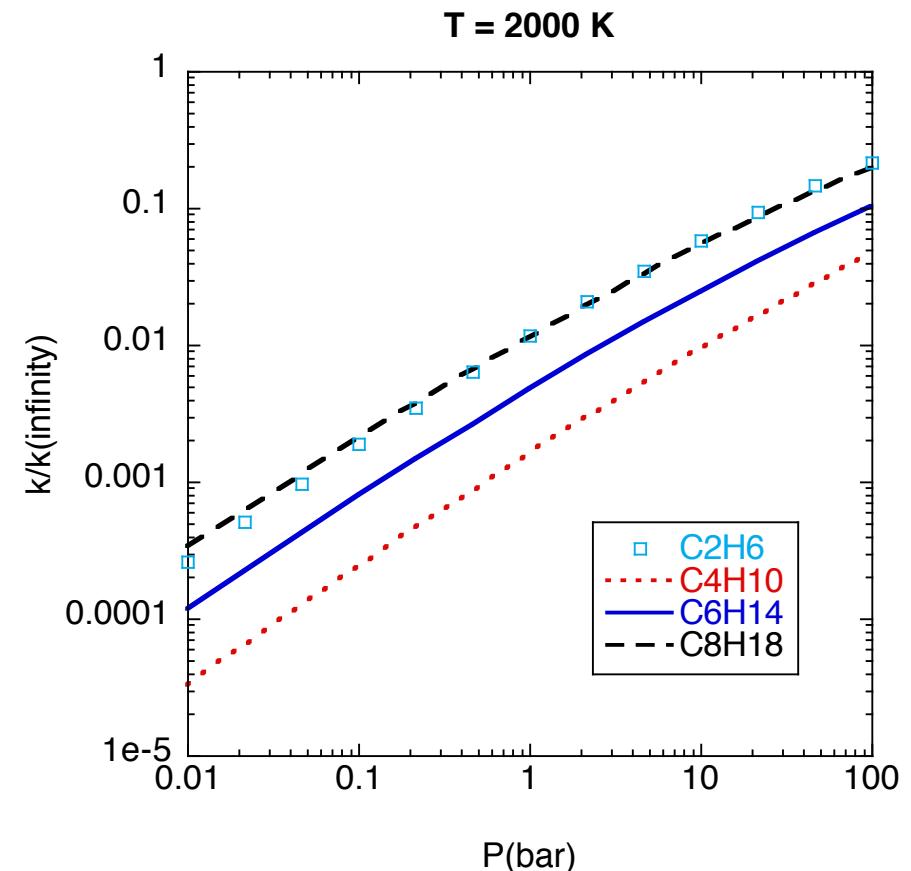
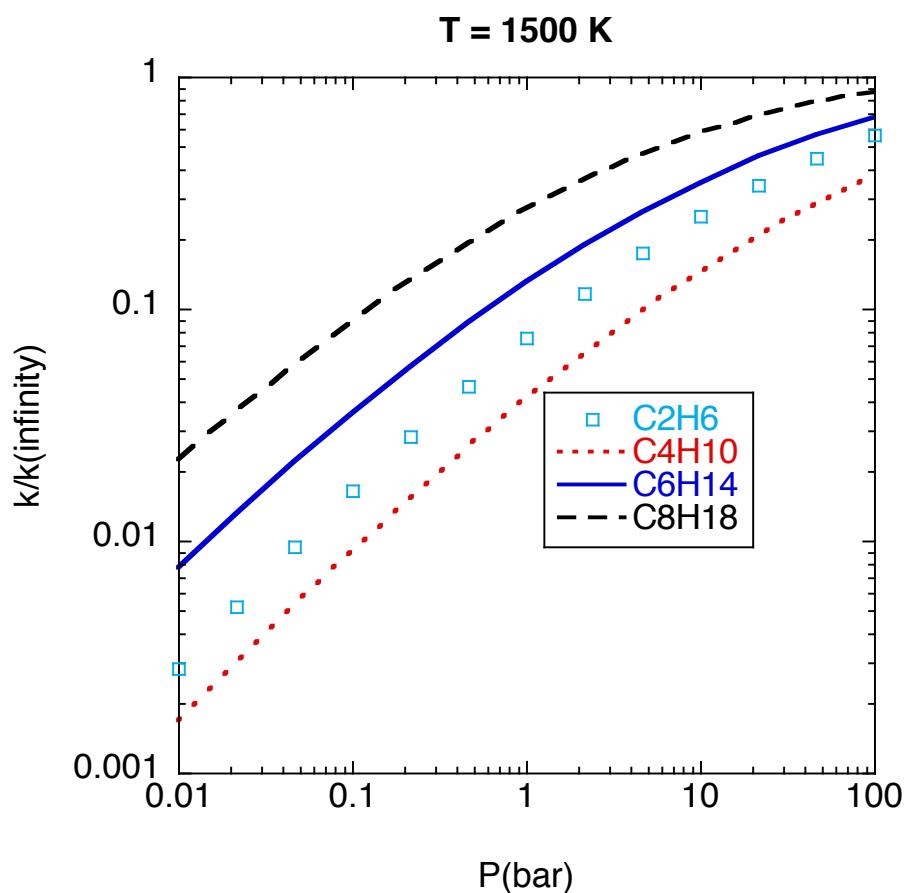
1. Pressure Dependent Rates
 - Size and T dependence
 - Ring formation reactions (Jim Miller)
 - Radical-complex mechanism (Amit Sharma)
2. Methanol Ignition (Rex Skodje, Mike Davis, Alison Tomlin, Larry Harding)
 - Extrapolate validated model outside validation range
 - Global uncertainty analyses => HO₂ reactions are key
3. H₂ and C₁-C₂ Combustion (Jeffery Santner, Mike Burke, Yiguang Ju, Fred Dryer)
 - Problems with modeling flame speeds at high pressure
 - HO₂, H₂O₂, and HCO
4. High T Combustion
 - Key is branching to H, CH₃, and C₂H₅ (Warnatz)
 - CH₃O₂, CH₃OOH (Pitz)
5. Low Temperature Combustion (Goldsmith, Green, Welz, Zador, Taatjes)
 - R+O₂, RO₂, QOOH



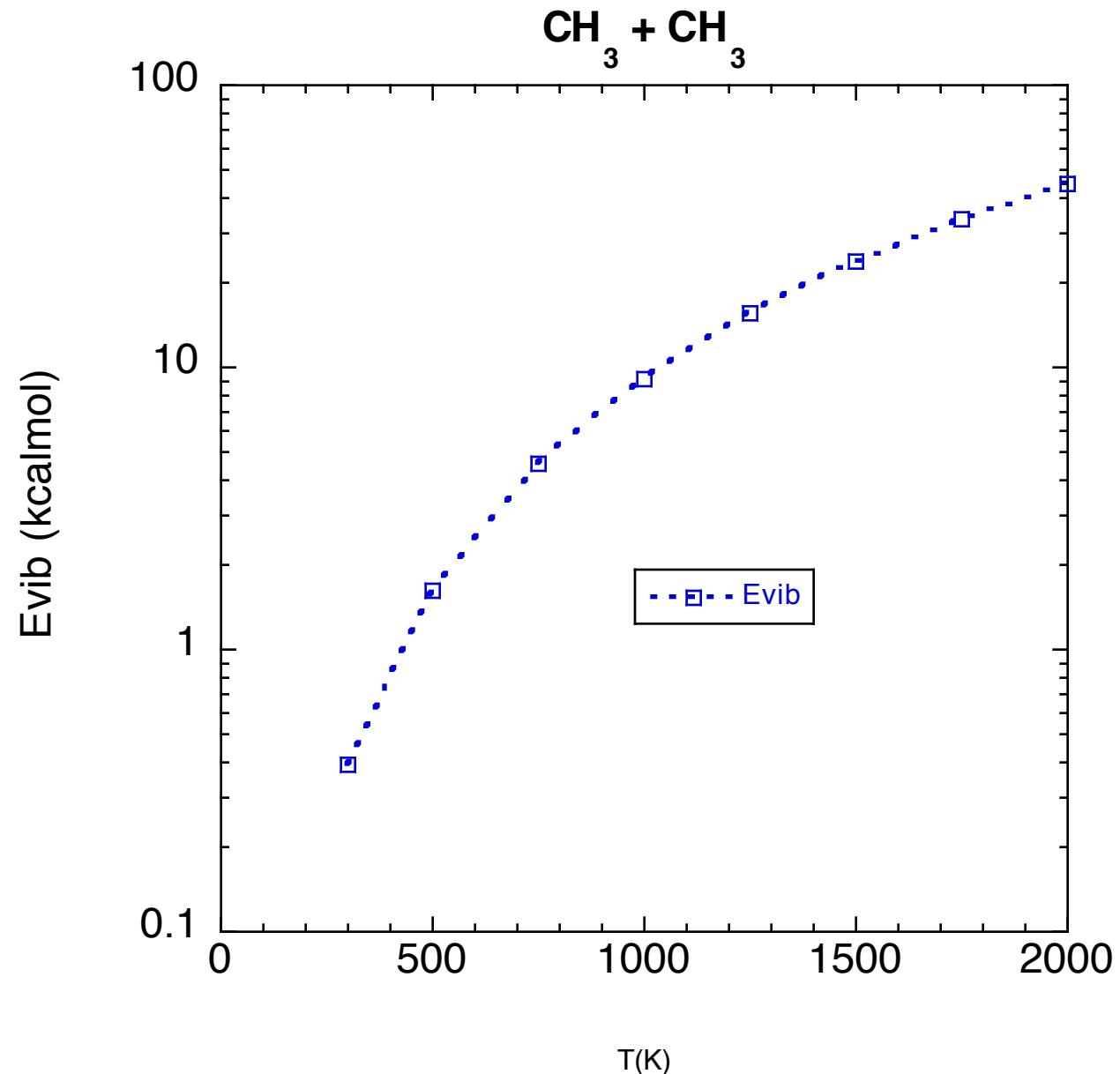
R_2 Dissociation Size and Pressure Dependence



R_2 Dissociation Size and Pressure Dependence



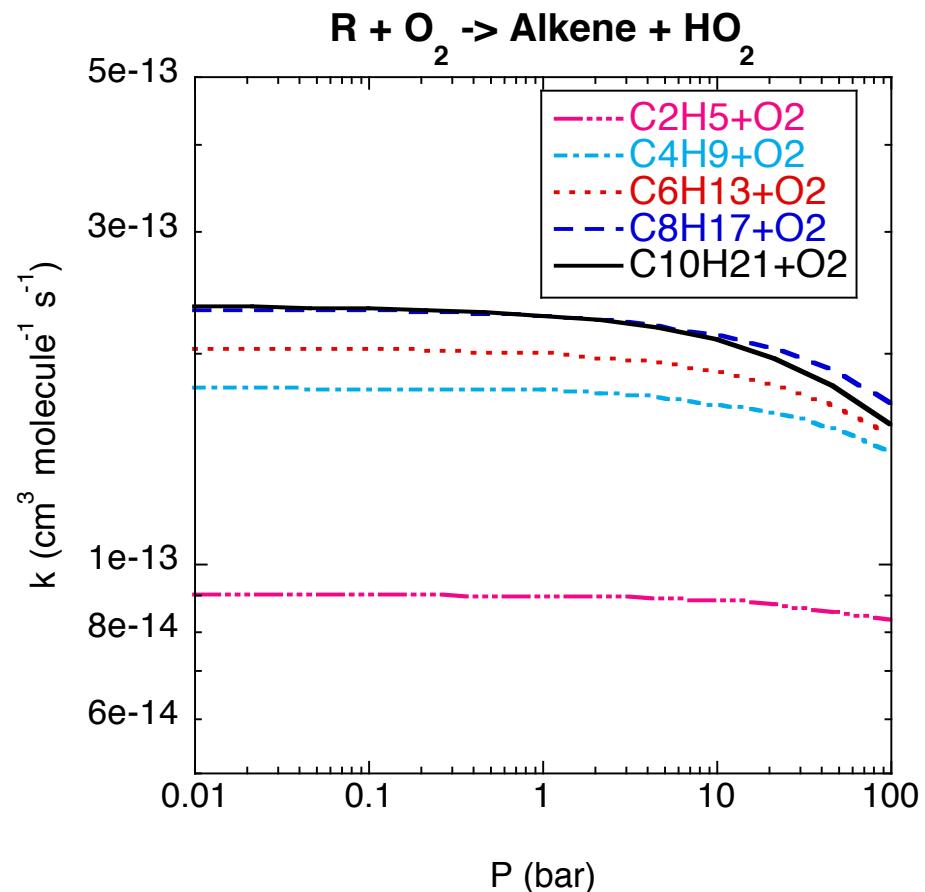
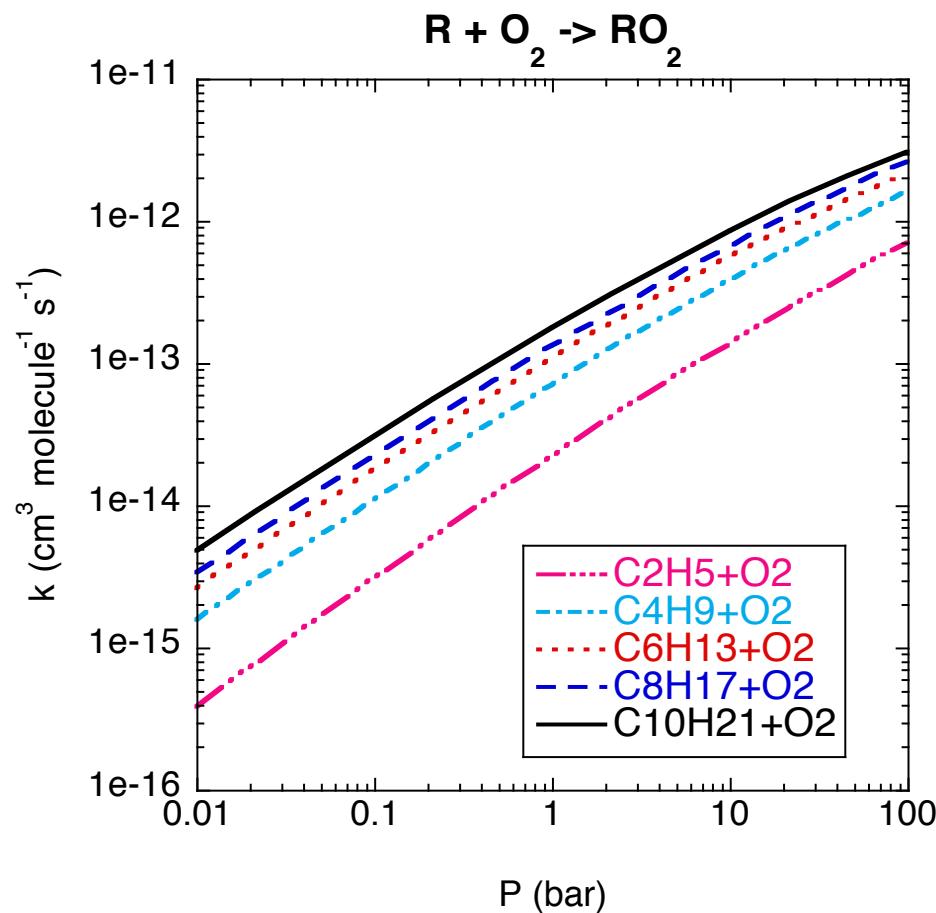
R₂ Dissociation Evib



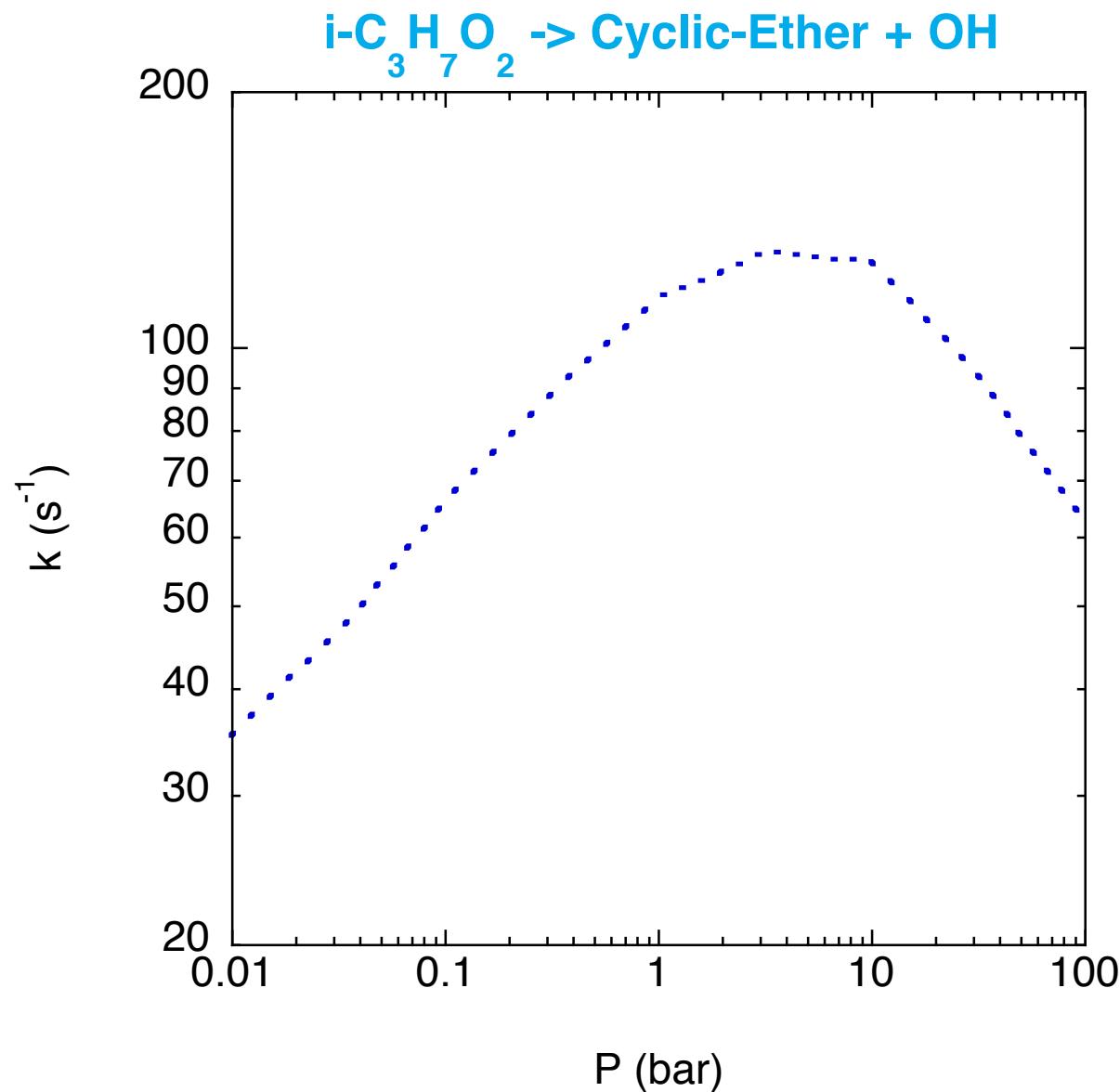
$R + O_2$

Size and Pressure Dependence

$T = 1000 \text{ K}$

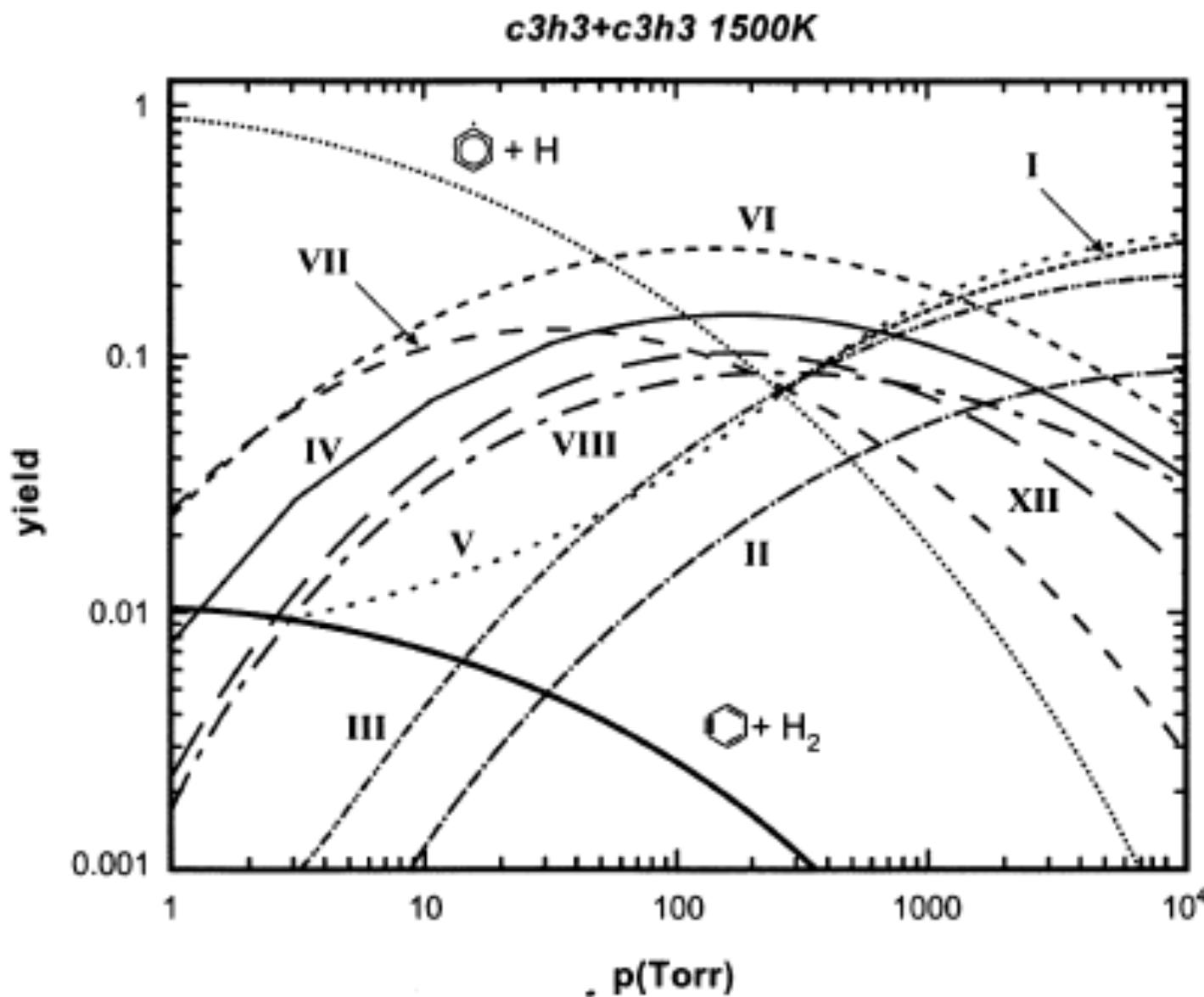


i-C₃H₇O₂ Nonmonotonic Pressure Dependence





Product Distribution

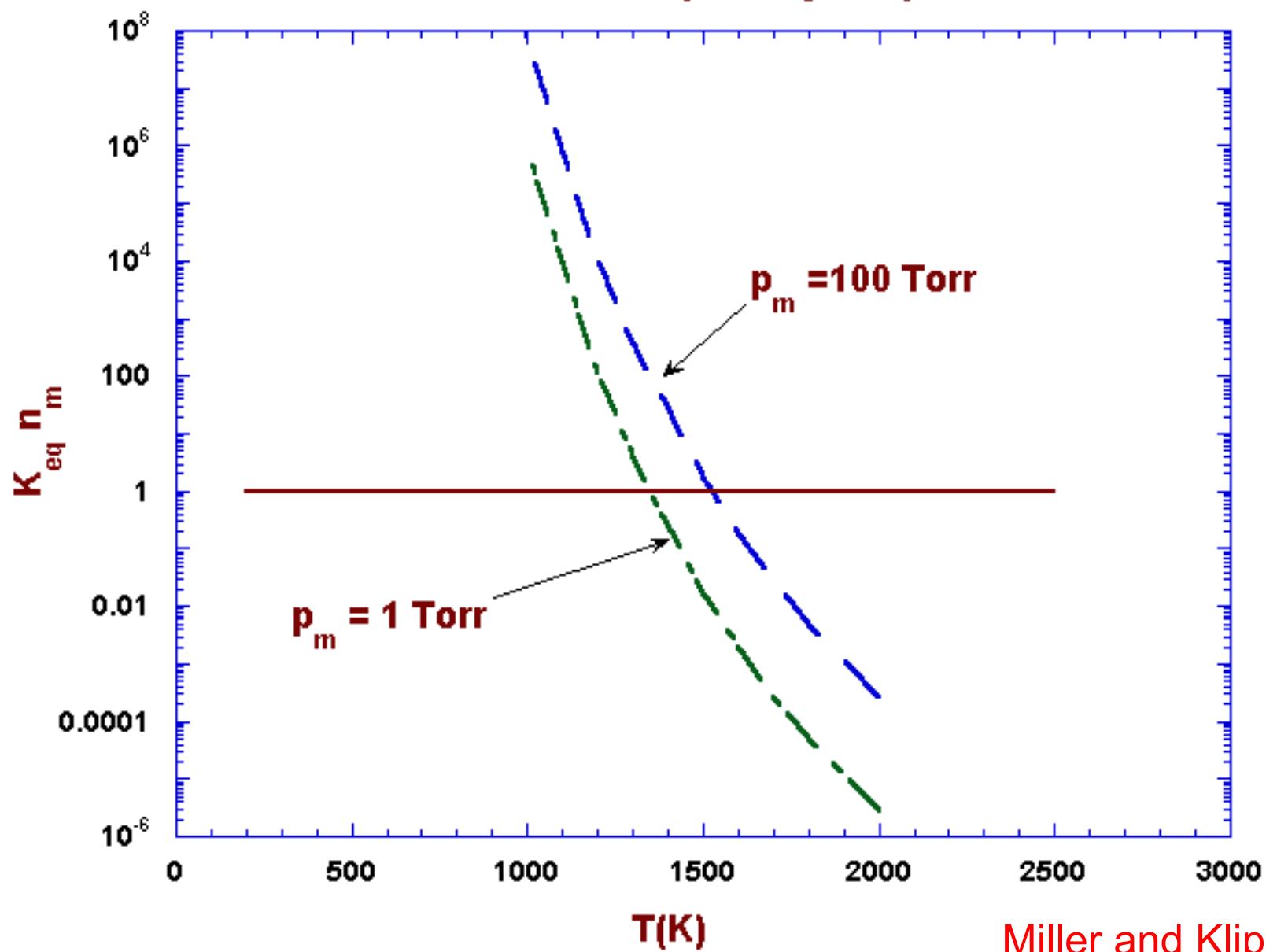


I,II,V=initial adducts
VII=Benzene
IV = Fulvene

Miller and
Klippenstein
J. Phys. Chem. A
107, 7783 (2003).



n-c4h3+c2h2 <-> phenyl equilibrium

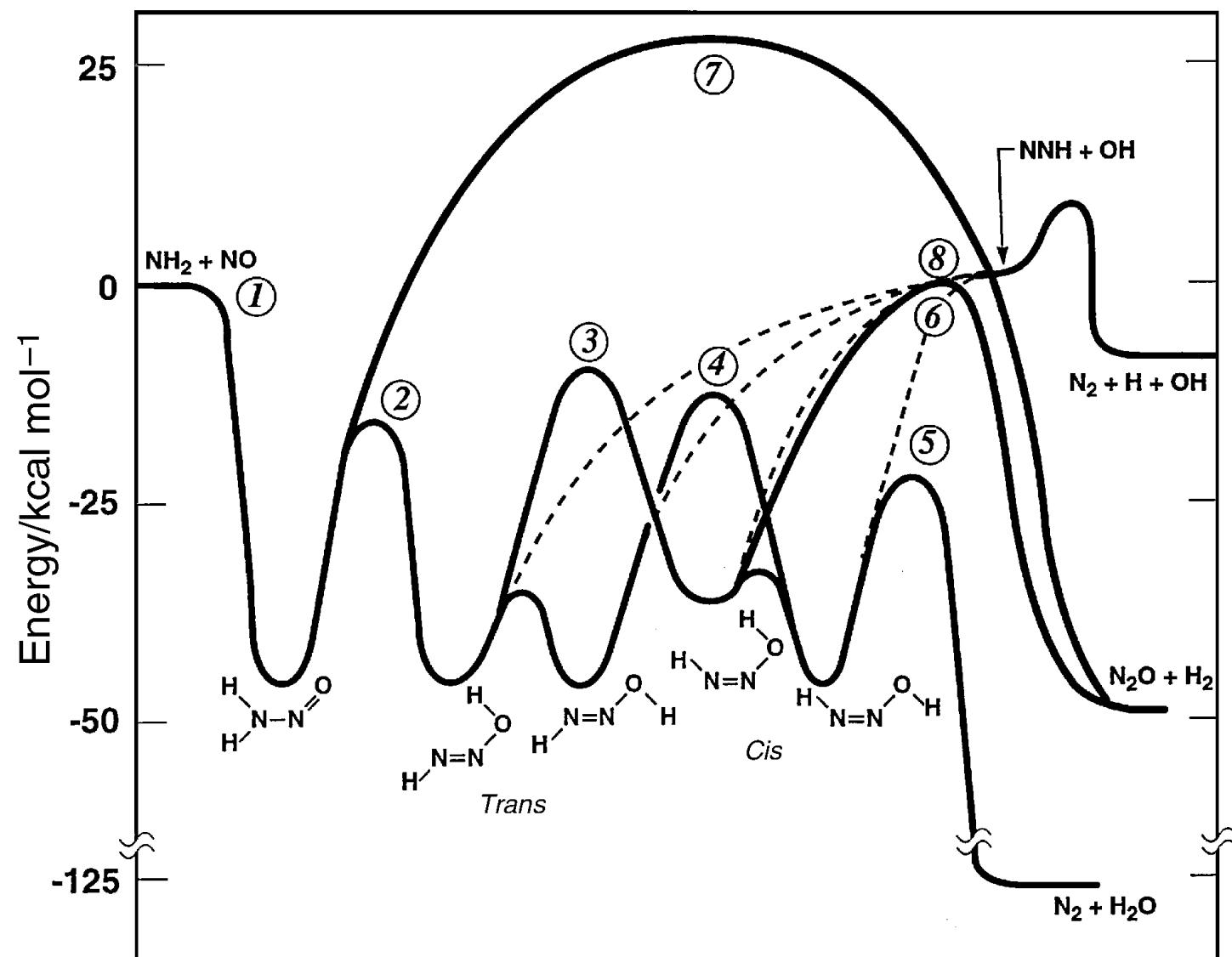


Miller and Klippenstein



Thermal DeNO_x

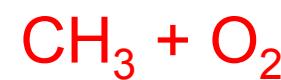
NH₂ + NO



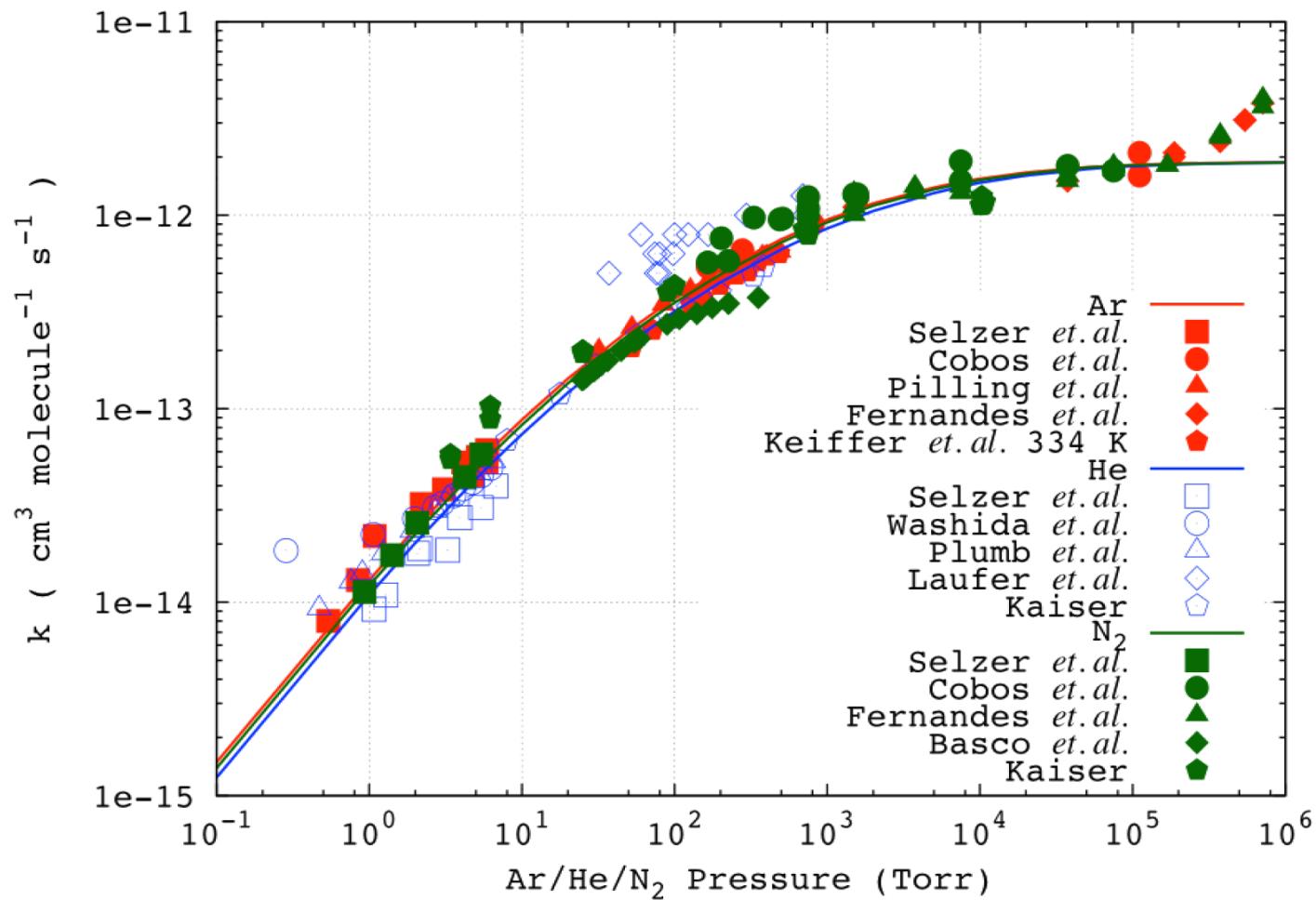
Miller and Klippenstein, J. Phys. Chem. A, 104, 2061, 2000



Beyond the High Pressure Limit



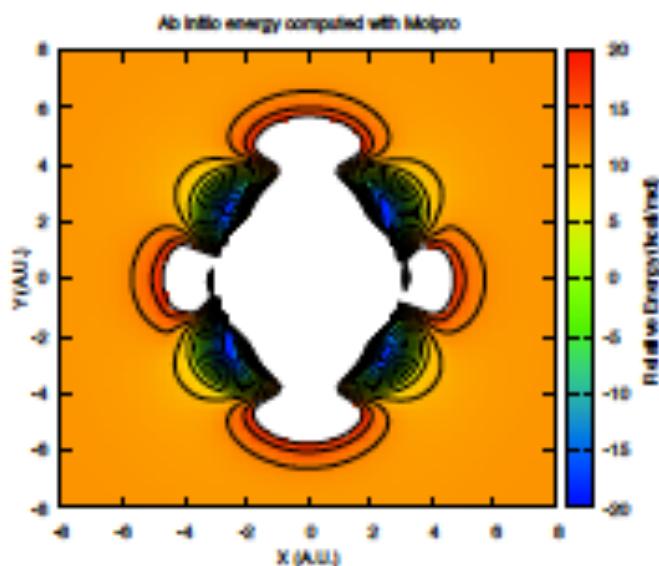
Amit Sharma



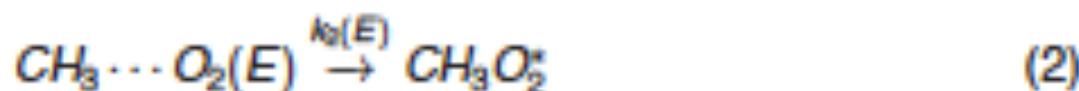
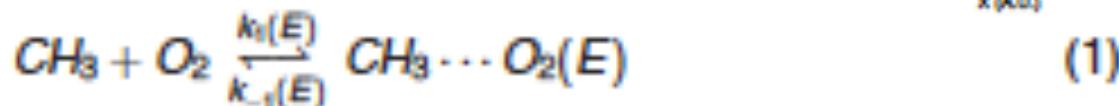
Fernandes, Luther, Troe, J. Phys. Chem. A, 114, 9963 (2010)



Two Transition States



Direct Mechanism



Using RRKM rates for individual reactions.

$$k_{\text{eff}} = \frac{1}{h Q_{CH_3+O_2}} \int dE N_1(E) \exp(-\beta E) \frac{N_2(E)}{N_1(E) + N_2(E)} \quad (3)$$

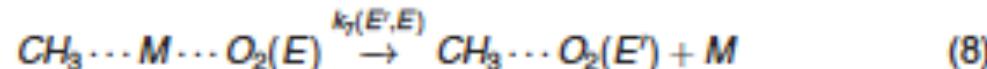
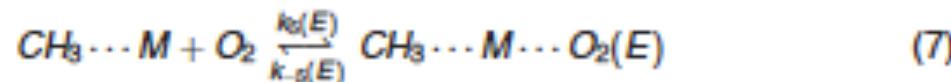
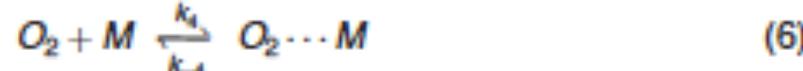
where, where ρ is the rovibrational density of states of reactant and N is the total number of available states of TS and we use

$$k_1(E) = \frac{N_1(E)}{h \rho_{A+B}} \quad k_2(E) = \frac{N_2(E)}{h \rho_{A-B}} \quad k_{-1}(E) = \frac{N_1(E)}{h \rho_{A-B}} \quad (4)$$



Radical-Complex Mechanism

R-C Mechanism We assume a reaction scheme wherein radical CH_3 reacts with rare-gas M to form a VDW complex ($[CH_3 \cdots M]$)



$$k_{\text{eff}} = \frac{1}{h Q_{CH_3+O_2}} \int dE N_1(E) \exp(-\beta E) \frac{N_2(E)}{N_1(E) + N_2(E)} + \\ \frac{k_3[M]}{k_{-3} h Q_{CH_3 \cdots M + O_2}} \frac{1}{\int_{-\infty}^{\infty} dE \frac{N_2(E)}{N_1(E) + N_2(E)}} \times \int dE' \frac{N_7(E, E') N_5(E') \exp(-\beta E')}{N_5(E') + \int dE N_7(E', E)} \quad (9)$$

(without $CH_3 \cdots M + O_2 \cdots M$ reaction)

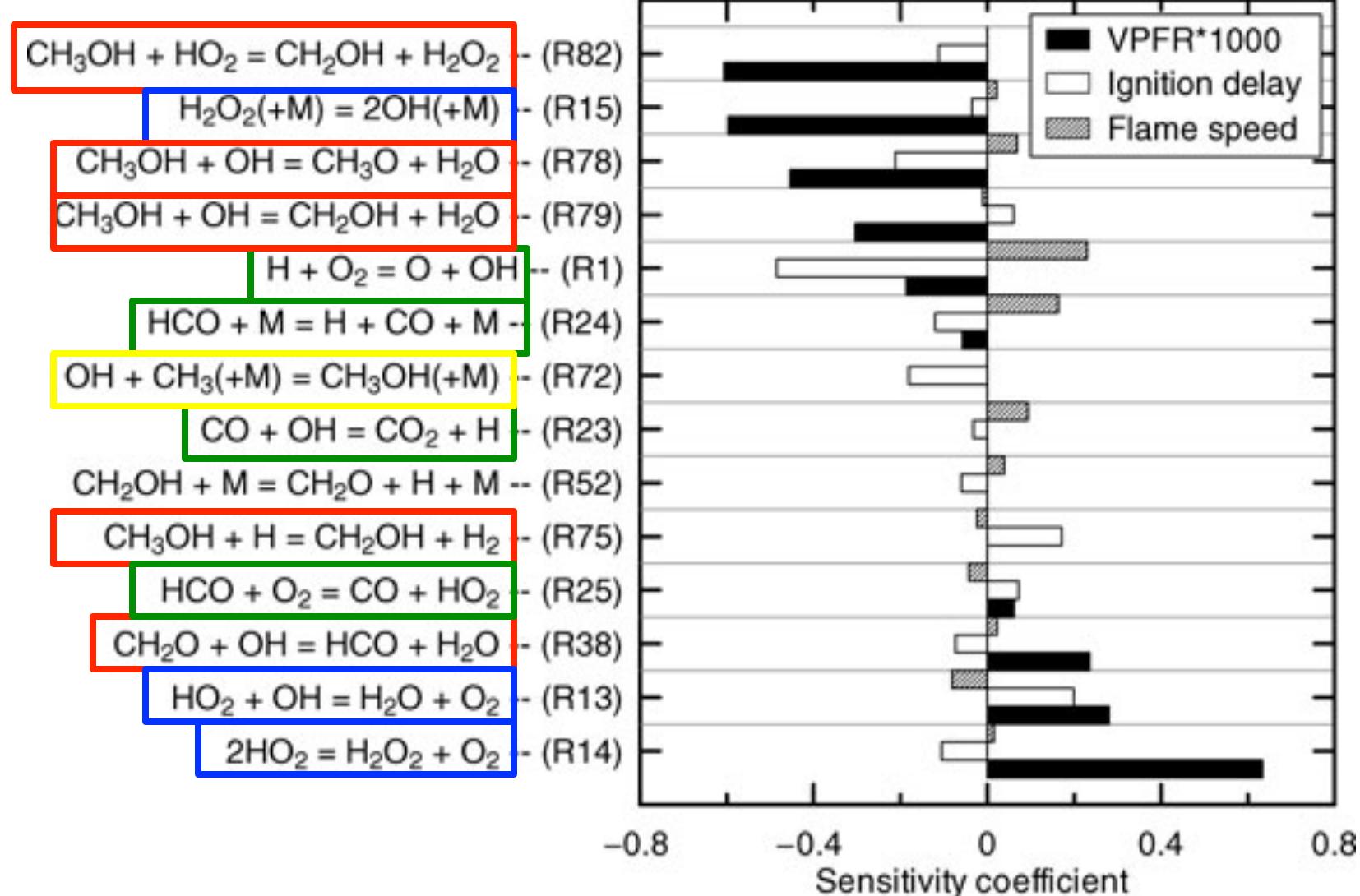


$$k_{\text{eff}} = \frac{1}{h Q_{CH_3+O_2}} \int dE N_1(E) \exp(-\beta E) \frac{N_2(E)}{N_1(E) + N_2(E)} + \\ \int_{-\infty}^{\infty} dE \frac{N_2(E)}{N_1(E) + N_2(E)} \times \int dE' \frac{N_7(E, E')}{N_5(E') + N_6(E') + \int dE N_7(E', E)} \\ \left(\frac{N_5(E') \exp(-\beta E') K_{\text{eq}, CH_3 \cdots M}}{Q_{CH_3 \cdots M + O_2}} + \frac{N_6(E') \exp(-\beta E') K_{\text{eq}, O_2 \cdots M}}{Q_{CH_3 + O_2 \cdots M}} \right) \quad (11)$$



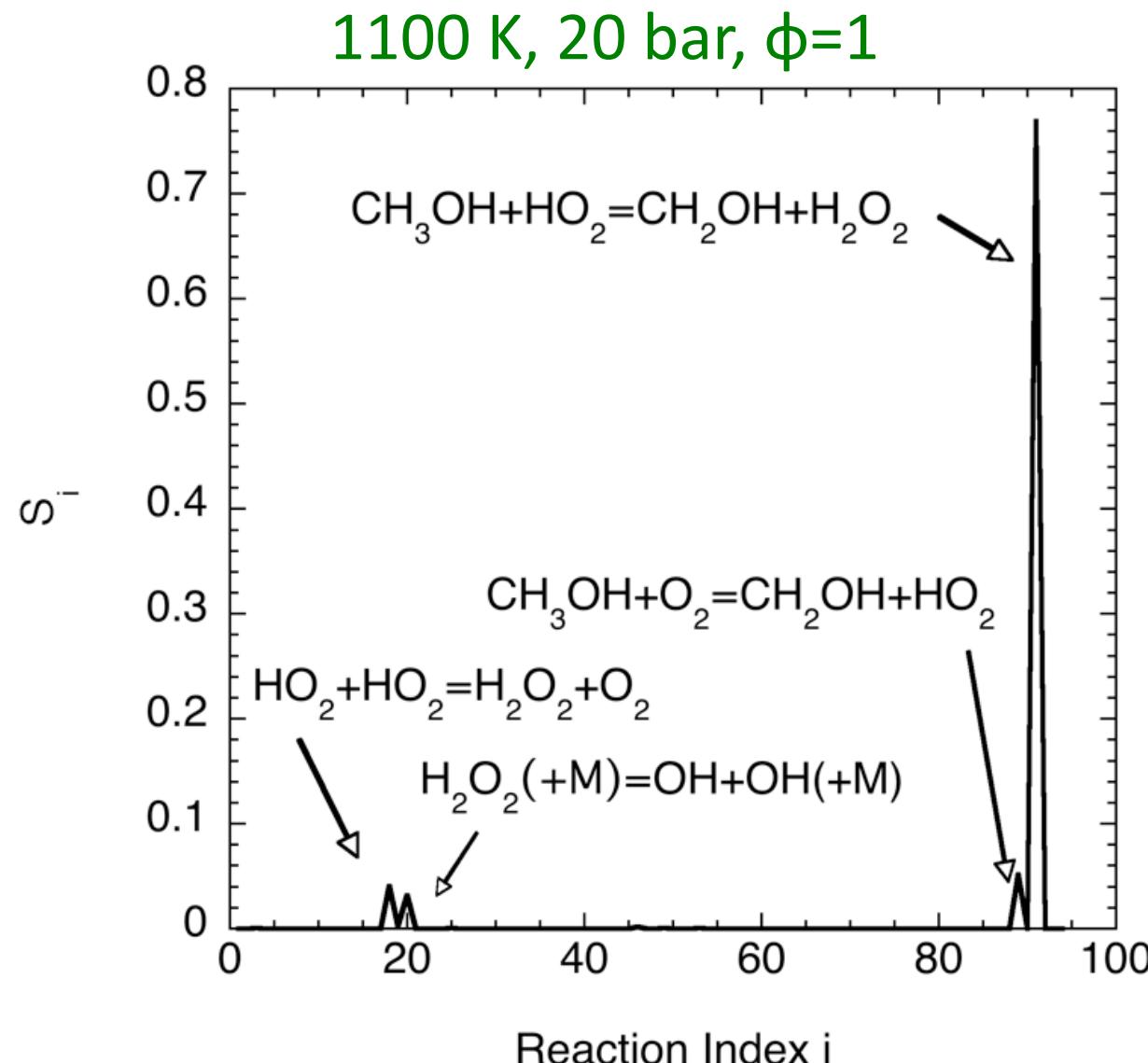
Sensitivity for Methanol (CH_3OH) Combustion

Li, Zhao, Kazakov, Chaos, Dryer, Scire, IJCK, 39, 109 (2007)



CH_3OH Combustion under Engine Conditions

Global Uncertainty Analysis for the Ignition Delay



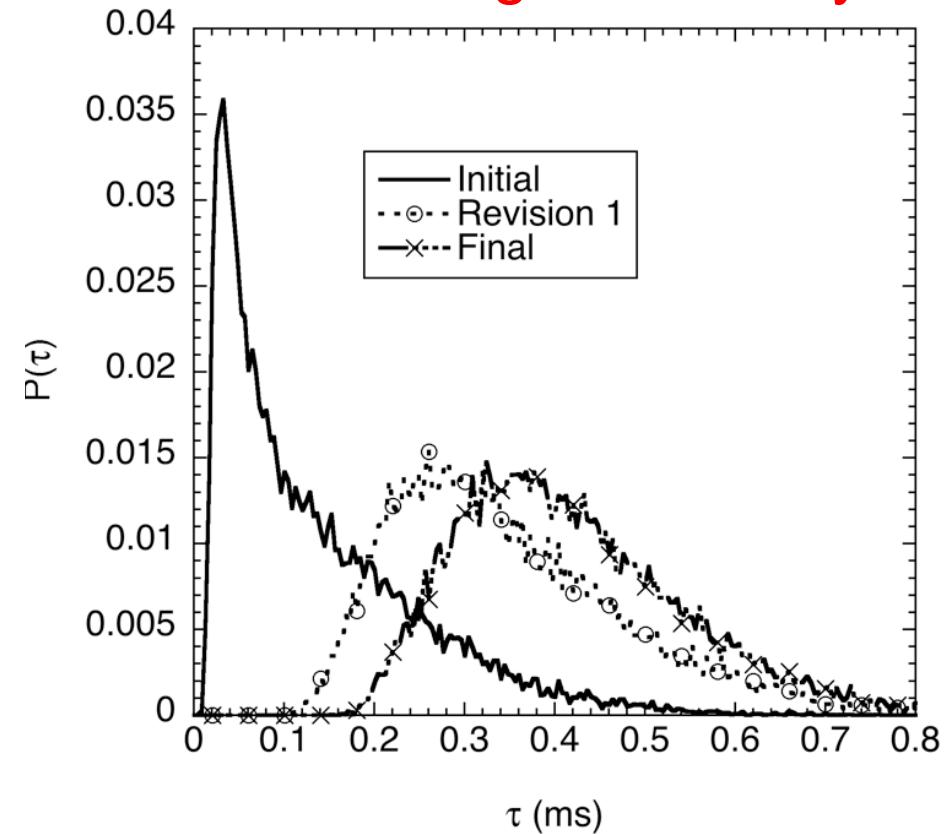
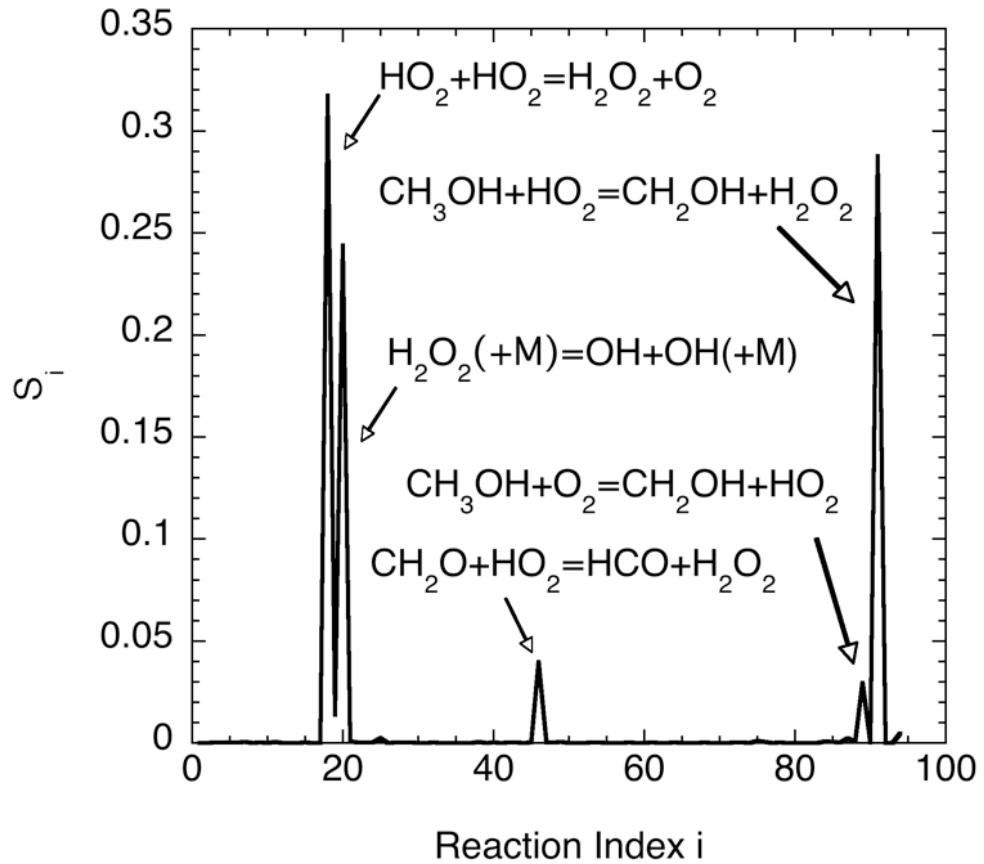
Klippenstein,
Harding,
Davis,
Tomlin,
Skodje
Proc. Comb.
Inst. 33, 351
(2011).



Change in ignition characteristics

Predicted Ignition Delays

Final Sensitivity Analysis



$\langle \tau \rangle$

Initial 0.11
Final 0.40

Width/ $\langle \tau \rangle$

Initial 2.0
Final 0.70



Why HO₂?

1. At High Pressure HO₂ is dominant radical

- H + O₂ = HO₂
- H + O₂ = O + OH
- HO₂ + H₂ = H₂O₂; H₂O₂ = OH + OH – Chain Branching

2. Large Uncertainty in HO₂ Rate Constants

- Hard to Study Fuel + HO₂
 - Large Barrier, Reaction Slow
 - At High T, HO₂ Decomposes
- Reverse Direction H₂O₂ + Radical
 - Also Large Barrier
 - H₂O₂ Also Decomposes – Makes 2 OH

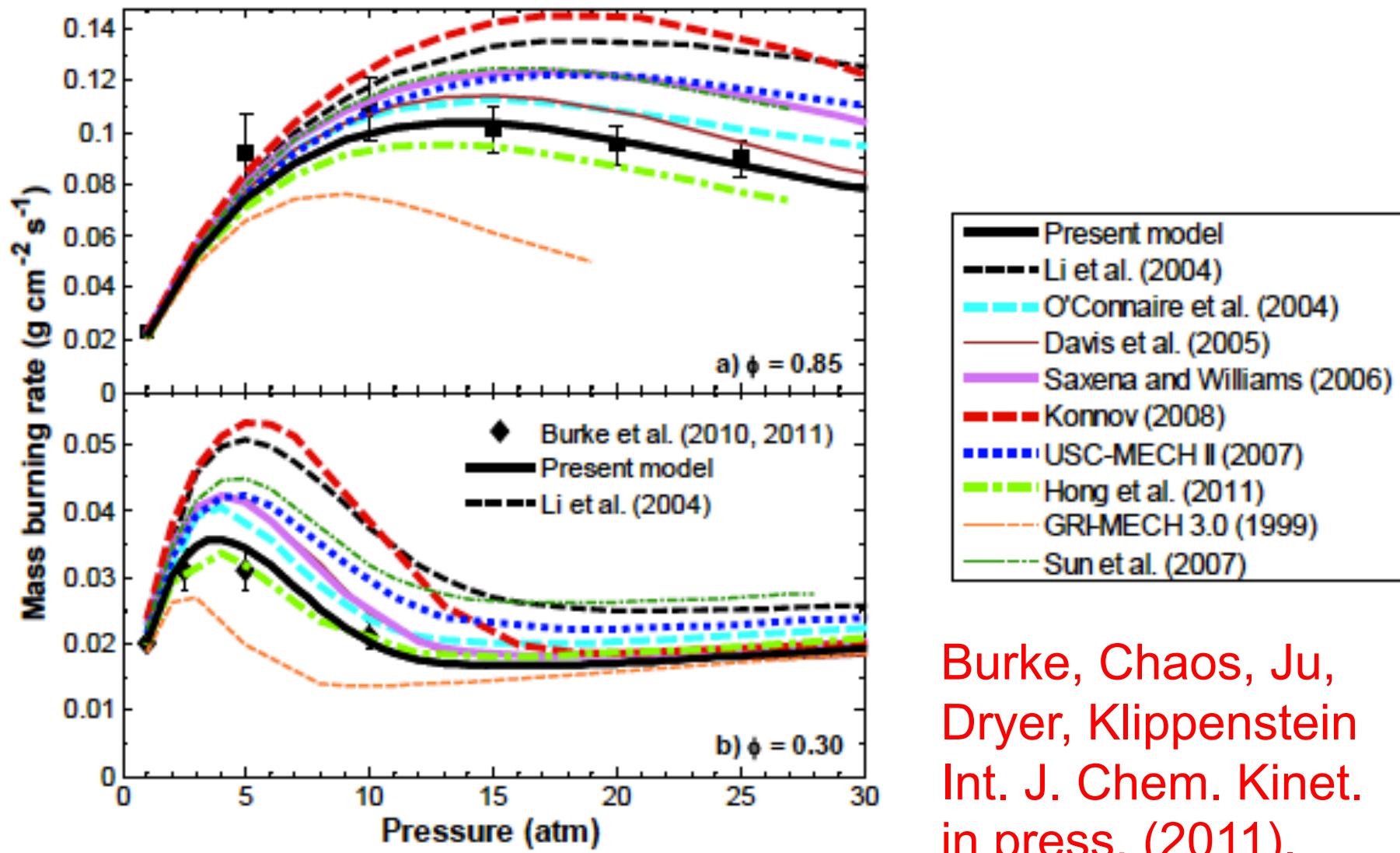
Experimental Probes

High Pressure – [HO₂] greater

Improved Shock Tube studies - Hanson



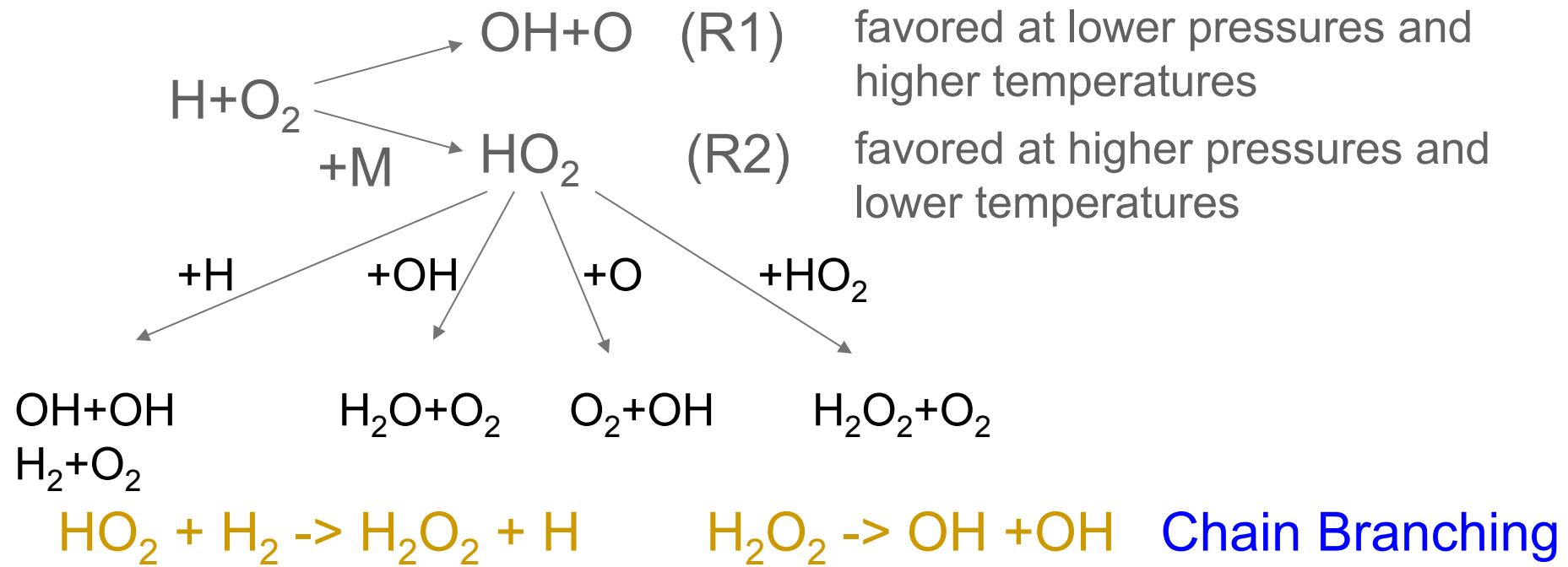
$\text{H}_2/\text{O}_2/\text{He}$ Mass Burning Rate



Burke, Chaos, Ju,
Dryer, Klippenstein
Int. J. Chem. Kinet.
in press, (2011).



Effect of Pressure on H₂ Kinetics



- HO₂ paths are active at high P's and T's
 - R1/R2 competition still controls pressure dependence
 - Responsible for *extended second limit* in homogenous kinetics

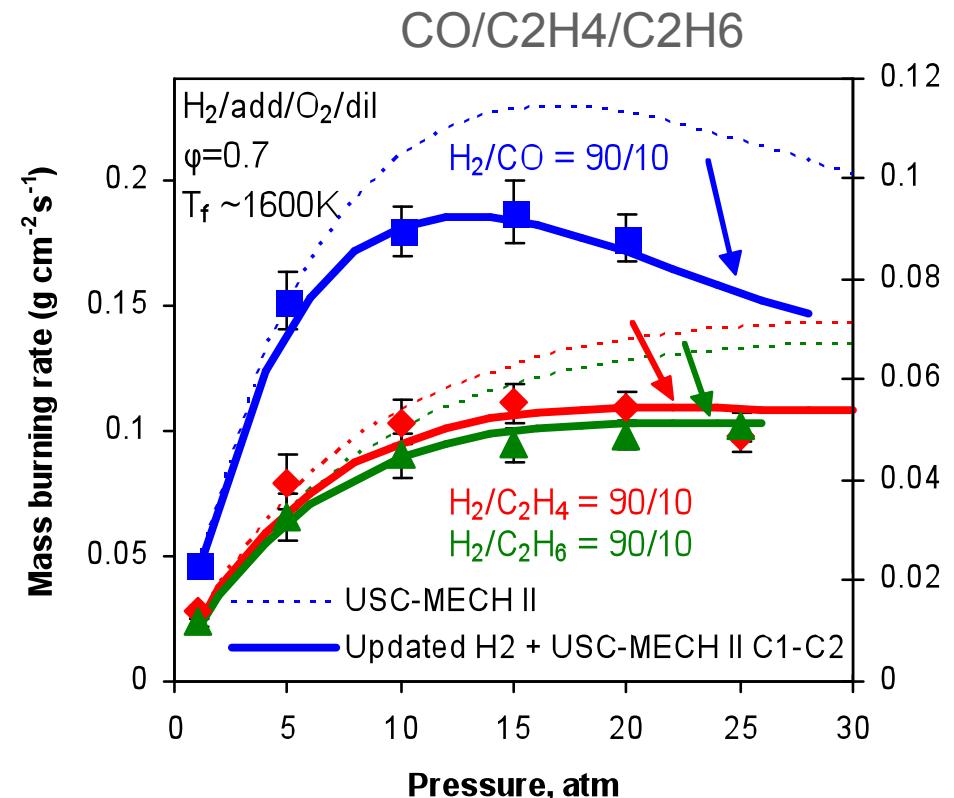
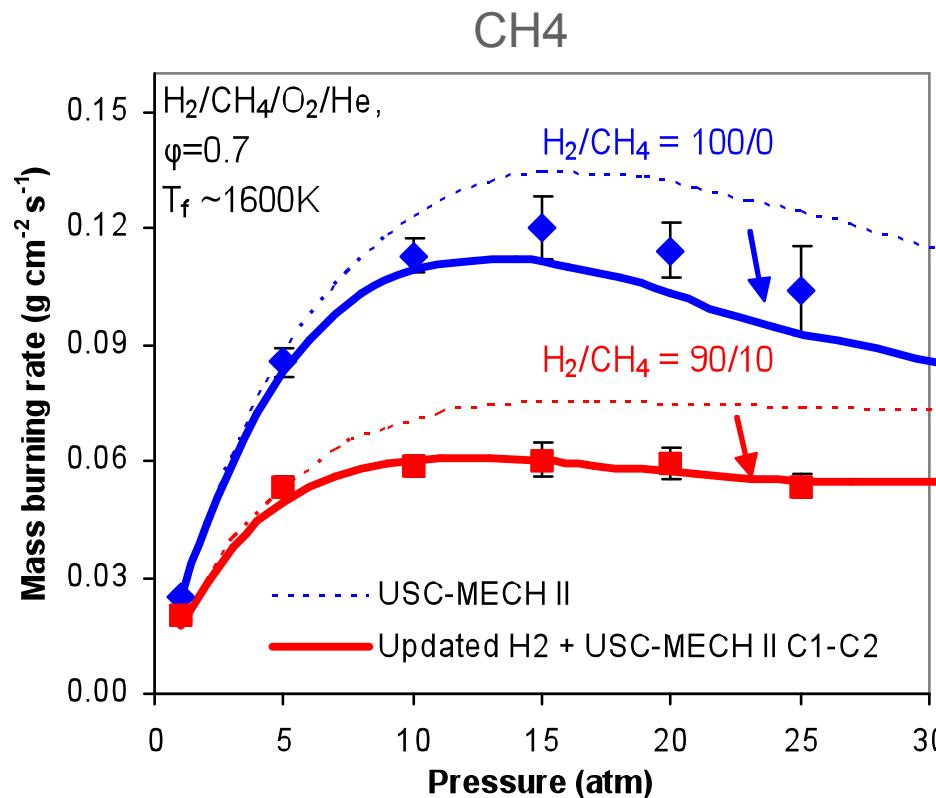
J. S. Santner, M. P. Burke, F. L. Dryer, Y. Ju

M.A. Mueller, T.J. Kim, R.A. Yetter, F.L. Dryer, *Int. J. Chem. Kin.*, 1999.

X. L. Zheng, C.K. Law, *Combust. Flame* 2004.



Improvements for high hydrogen C₁-C₂ flames



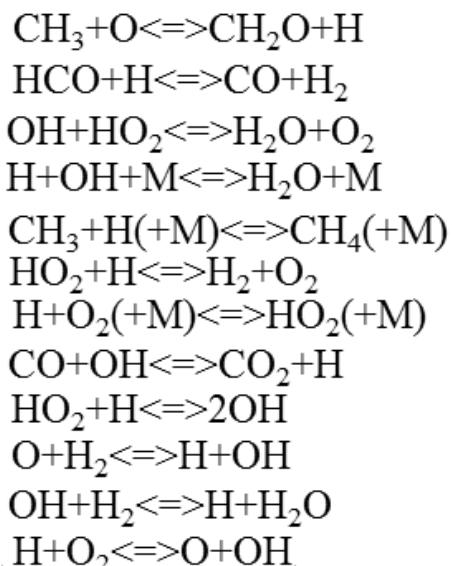
Updated H₂ model improves burning rate predictions for doping with CO, CH₄, C₂H₄, and C₂H₆

M.P. Burke, F.L. Dryer, Y. Ju, *Proc. Comb. Inst.* (2010) in press.
J. S. Santner, M.P. Burke, F.L. Dryer, Y. Ju, in preparation.



Mass Burning Rate Sensitivities: Doped Flames

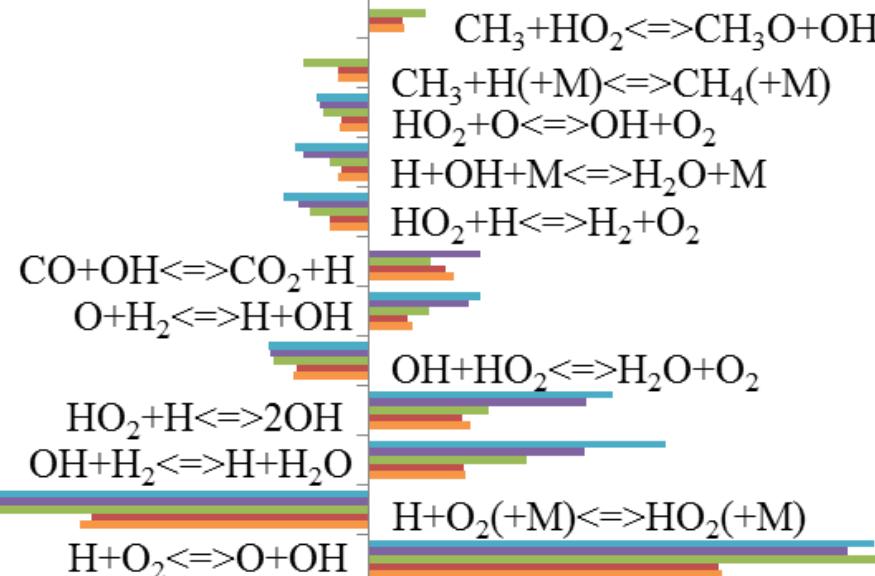
1 atm



- H_2
- H_2/CO
- H_2/CH_4
- $\text{H}_2/\text{C}_2\text{H}_6$
- $\text{H}_2/\text{C}_2\text{H}_4$

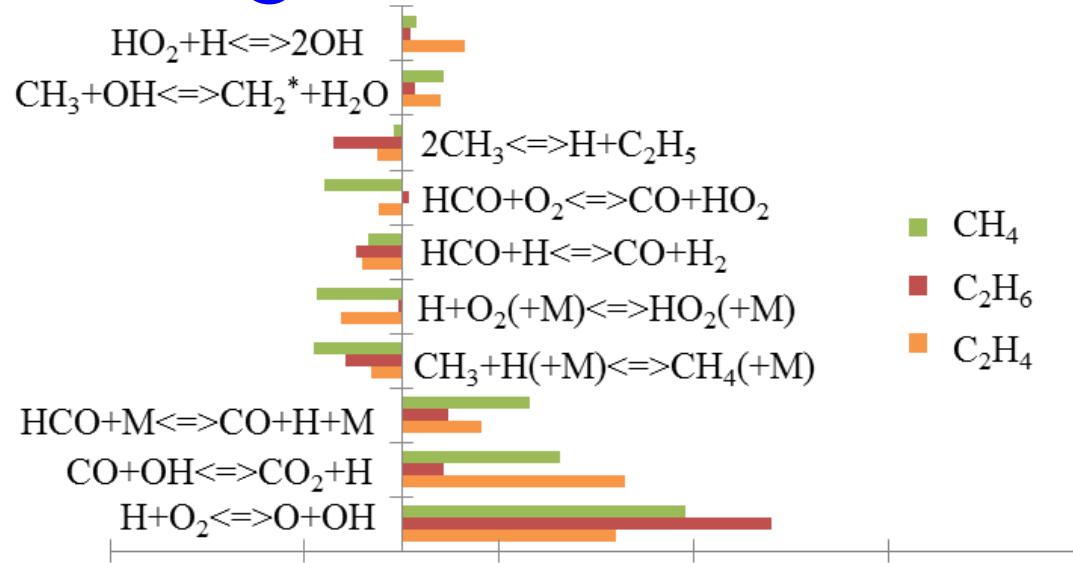
Santner, Burke,
Dryer, Ju

20 atm



Sensitivity Coefficient

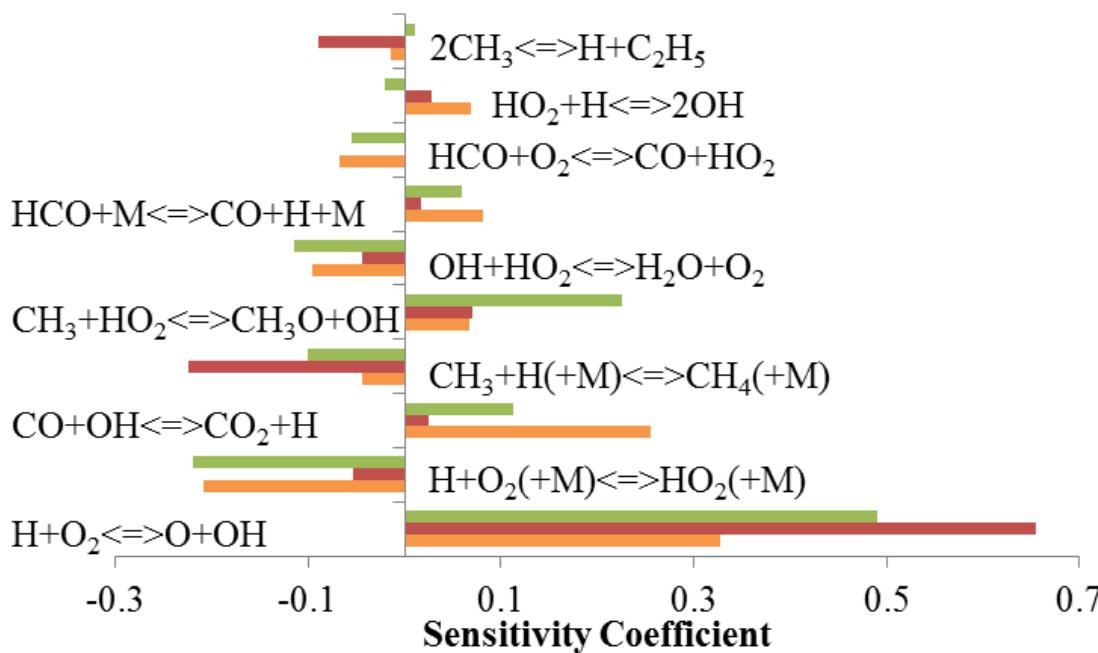
Mass Burning Rate Sensitivities: Pure C1-C2



Santner, Burke,
Dryer, Ju

$T_f = 1800 \text{ K}$

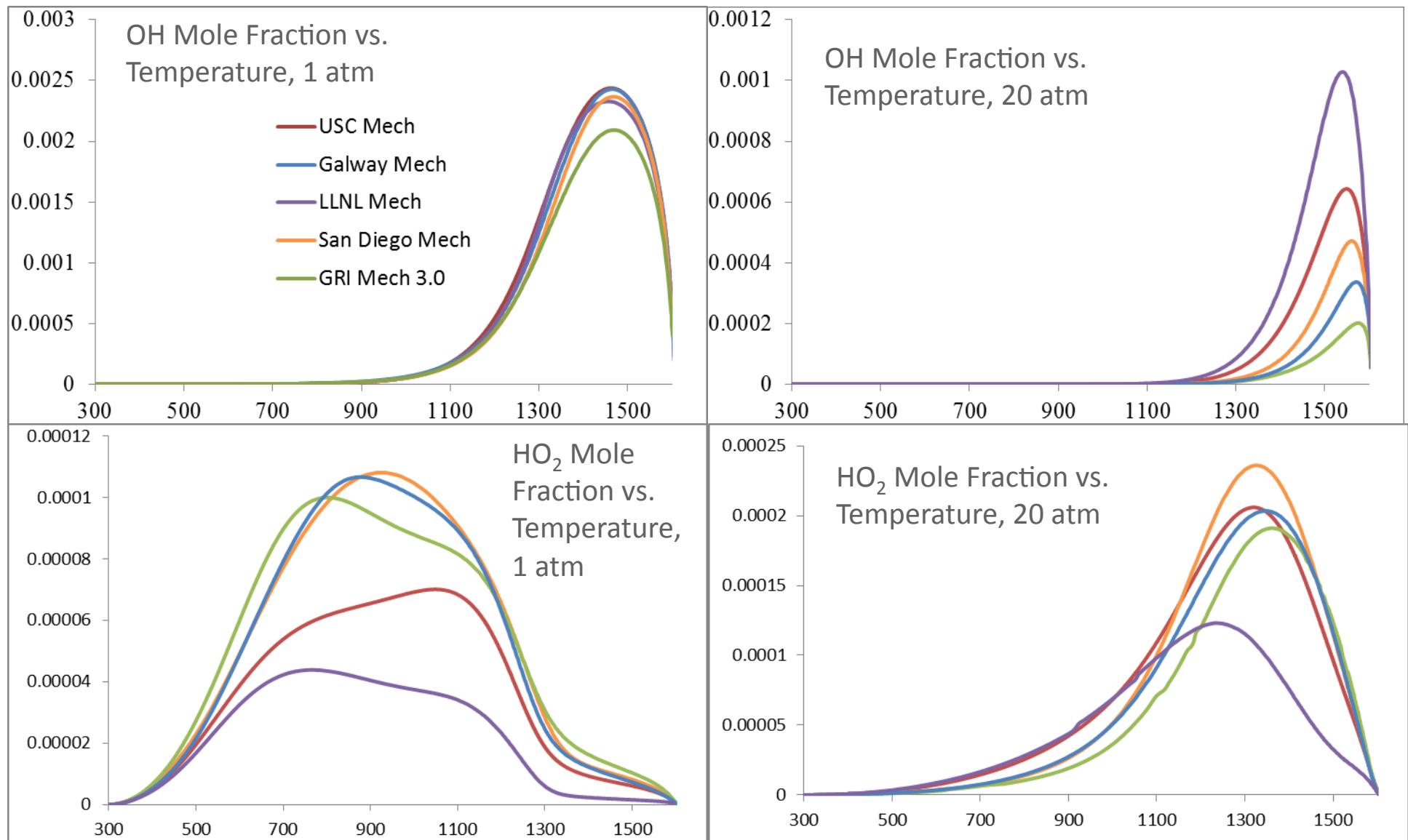
$P = 1 \text{ atm}$



$P = 20 \text{ atm}$

Effect of Pressure and Model Variation on Radical Profiles - $\text{H}_2/\text{C}_2\text{H}_6$

Santner, Burke,
Dryer, Ju



High T

Decomposition of Fuel to Products is Rapid



Fuel Decomposition – more important for oxygenated fuels

Fuel Radical \rightarrow Products

Fuel Radical + O₂ \rightarrow Low Temperature Combustion

What matters is final branching to (Warnatz)

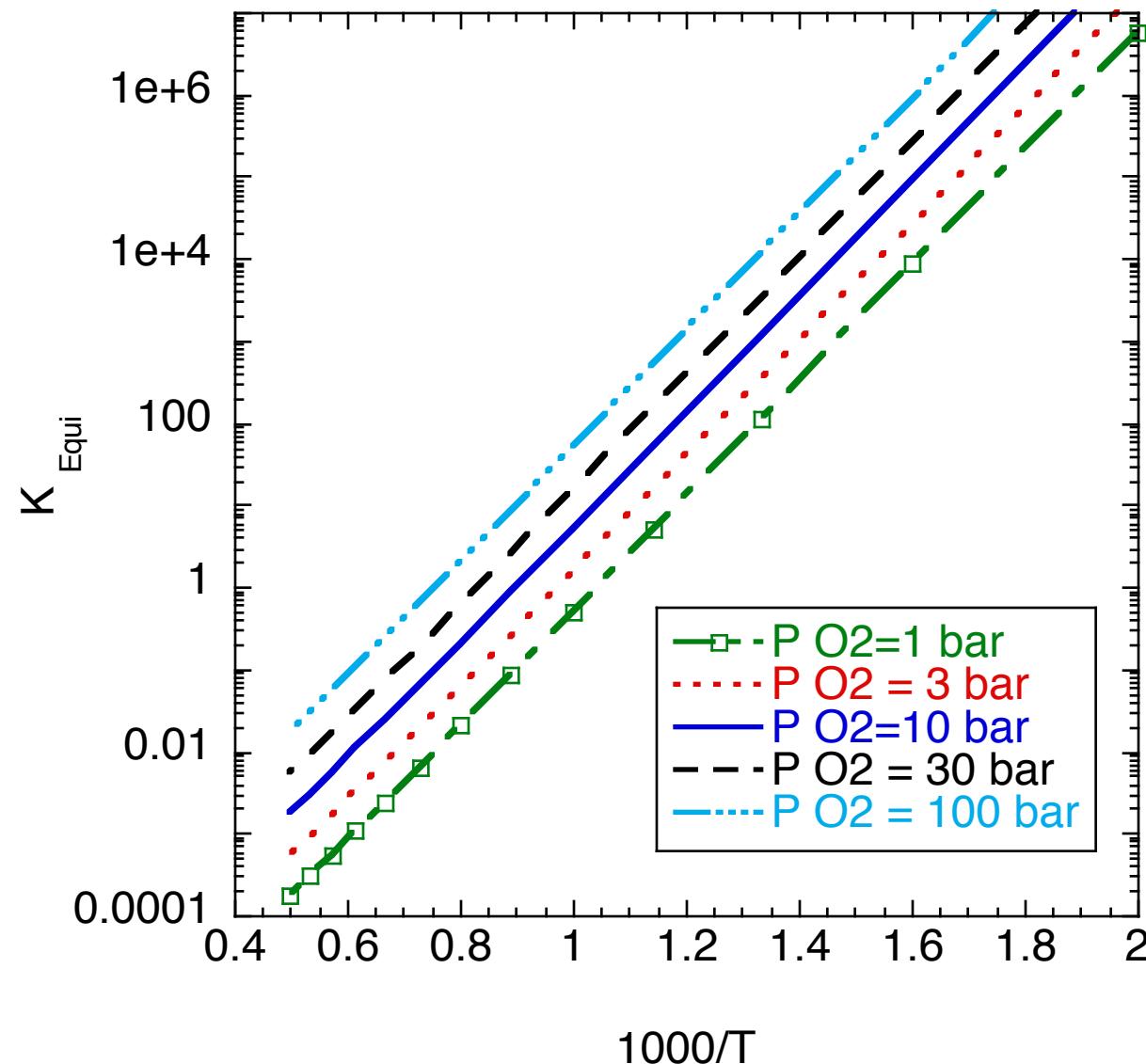
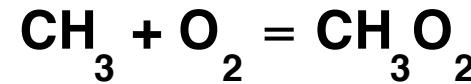


H vs CH₃ determines flame speed

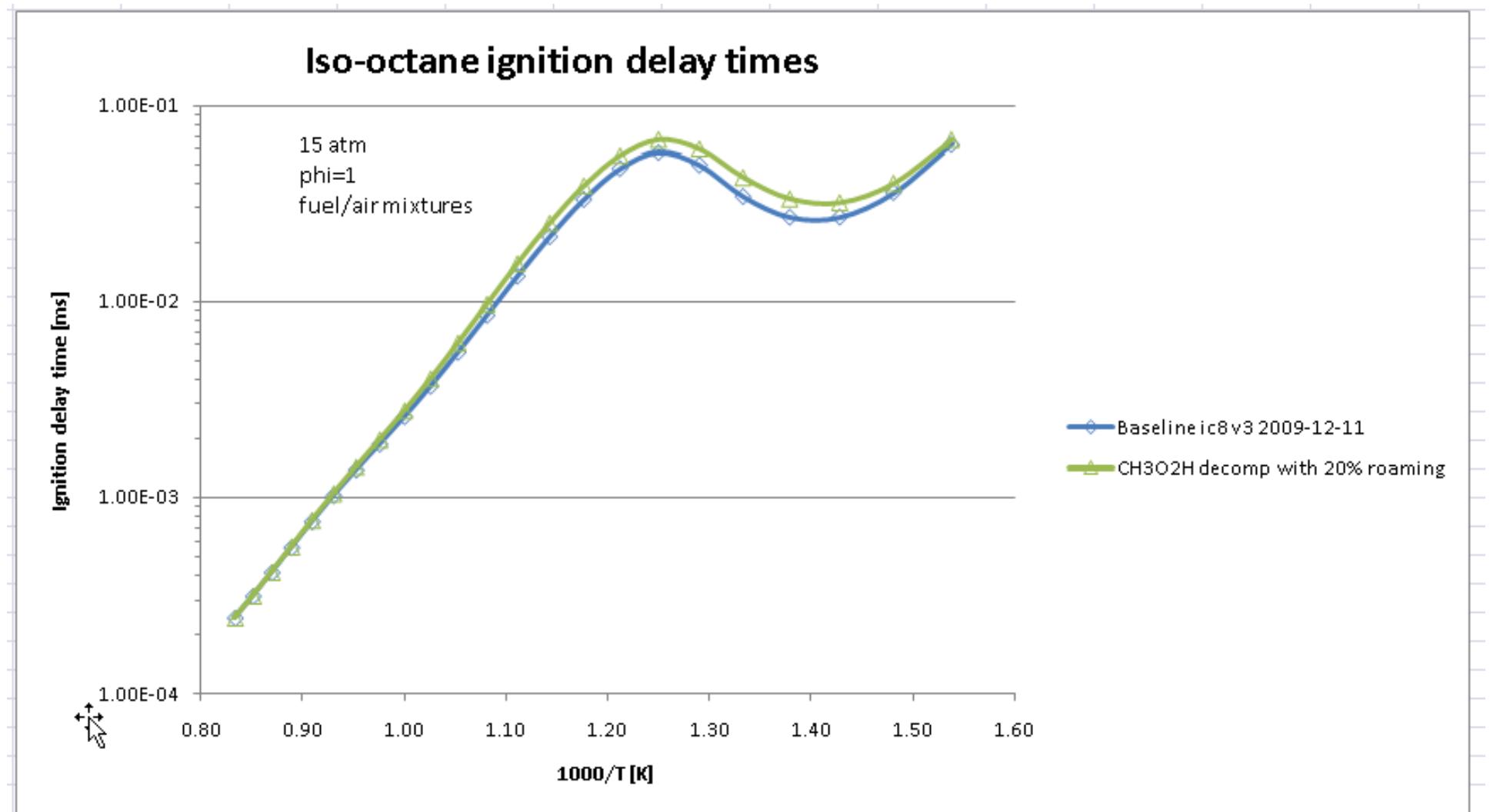
C₂H₅ and C₂H₃ contribute to soot growth



CH_3O_2 Equilibrium Constant



Effect of Roaming on Iso-octane Ignition Delays



William J. Pitz



Product Branching in HO₂ + Fuel

C₃H₈ Ignition

Global Uncertainty Analysis (Davis, Skodje, Zhou)

C₃H₈ + HO₂ is key



C₄H₉OH Combustion

C-EFRC

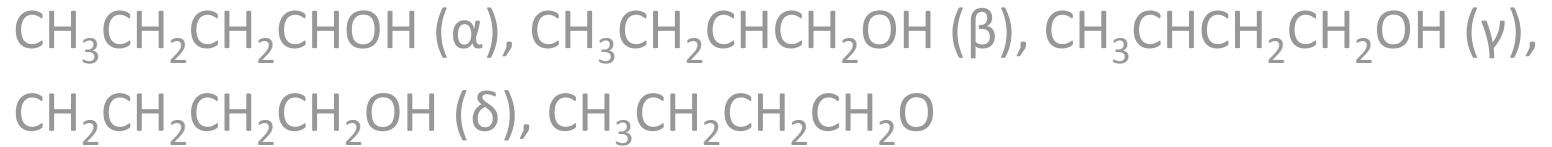
Flame Speeds, Extinction Curves, Species Profiles

Ignition Delays in Shock Tubes and RCM, Elementary Rate Coeff.

Species Profiles in Flames, Flow Reactors, and Shock Tubes

Global Uncertainty => C₄H₉OH + HO₂ is key (Davis, Skodje, Zhou)

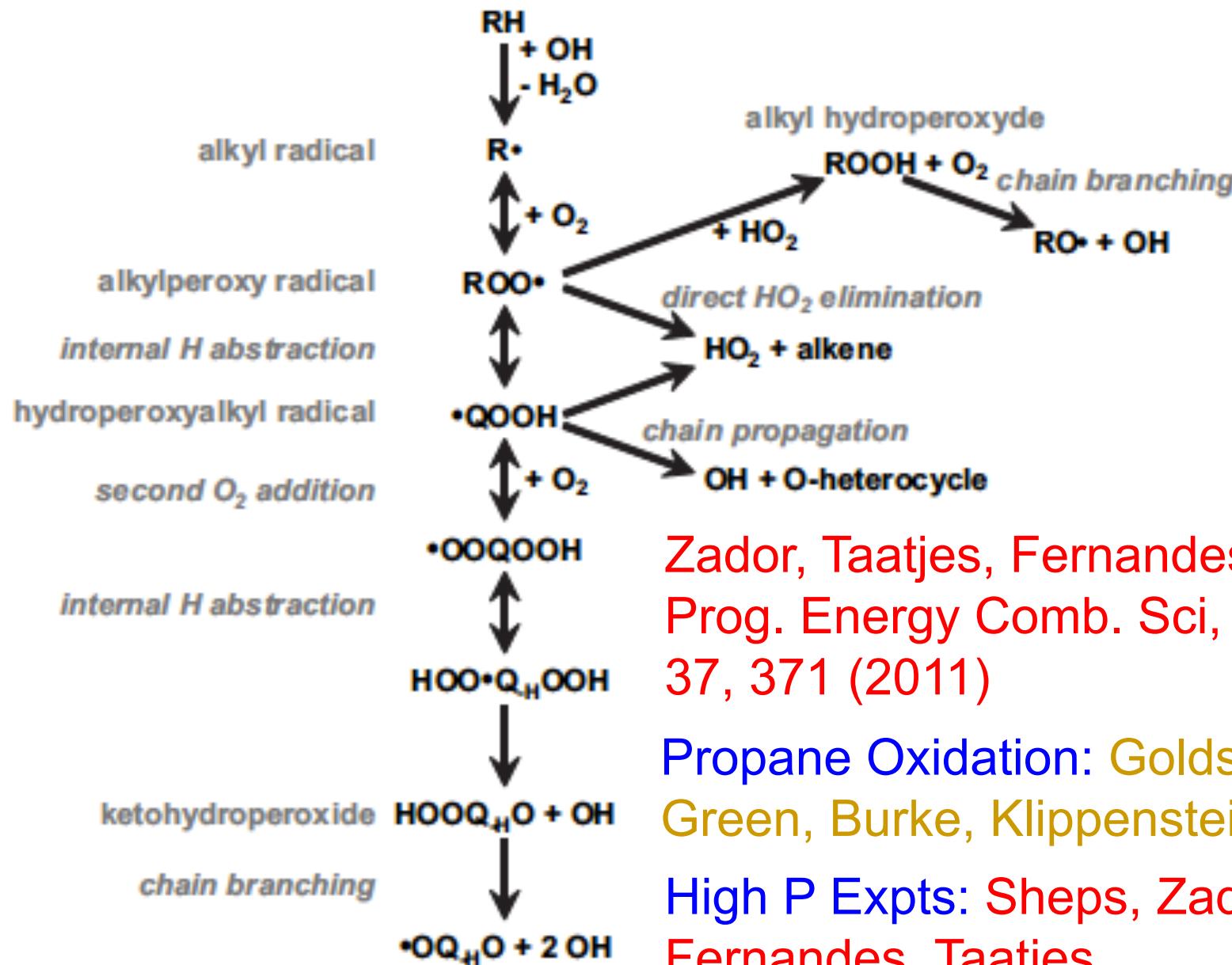
Theory (Taatjes, Curran, Truhlar)



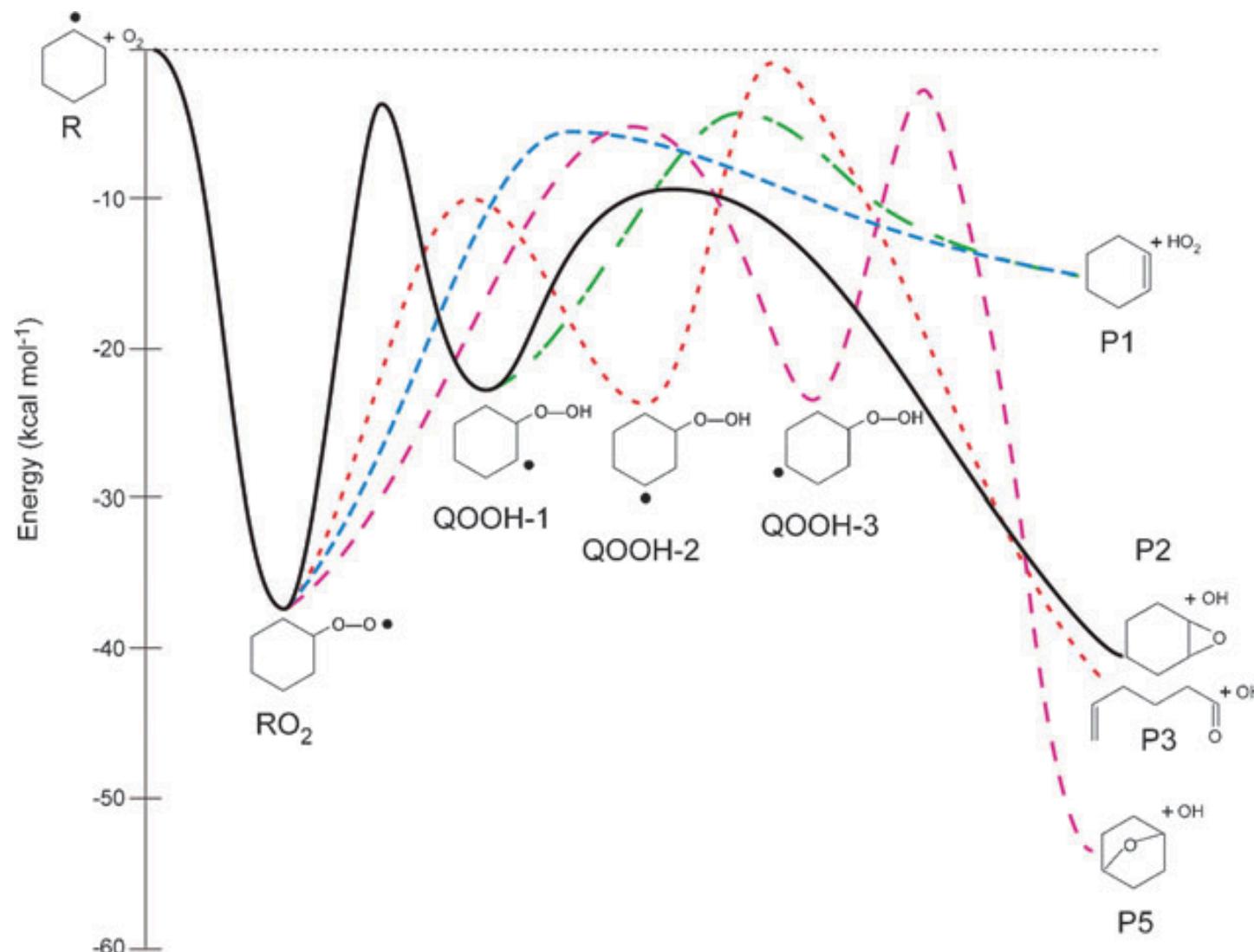
Hydrogen bonding in TS complicates theoretical analysis



Low Temperature Fuel Chemistry



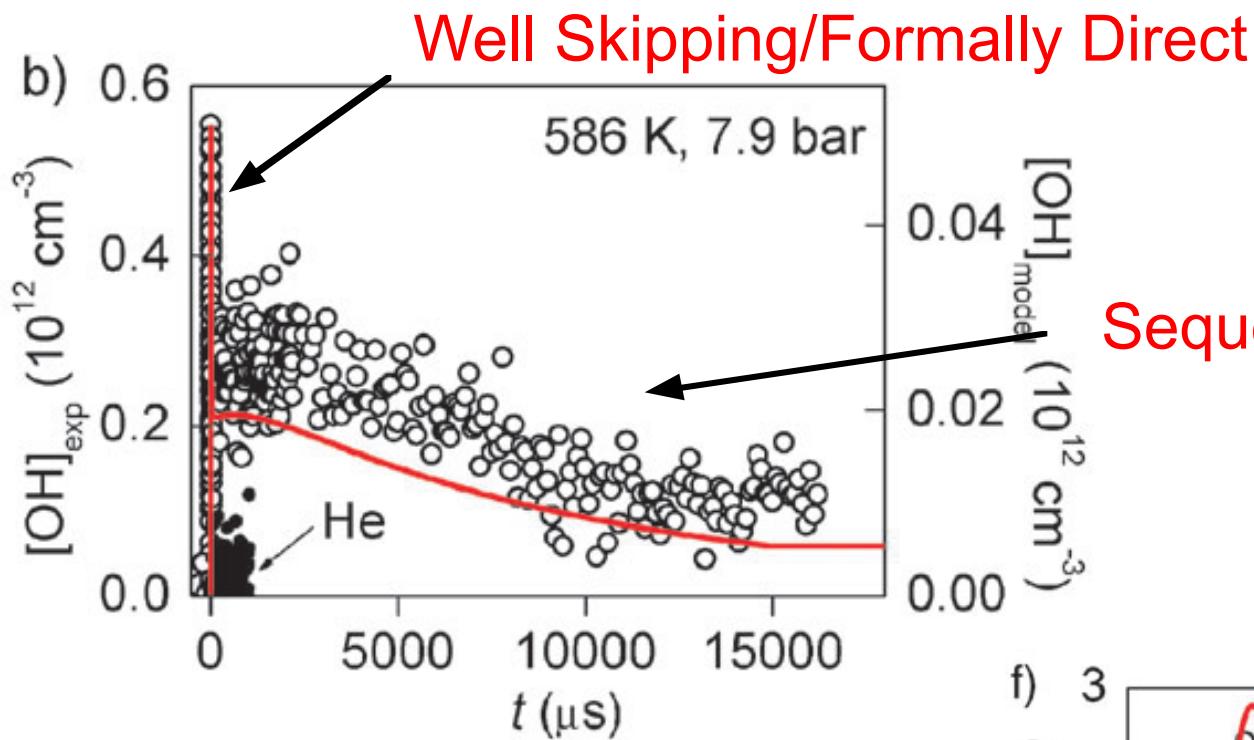
Cyclohexyl Oxidation



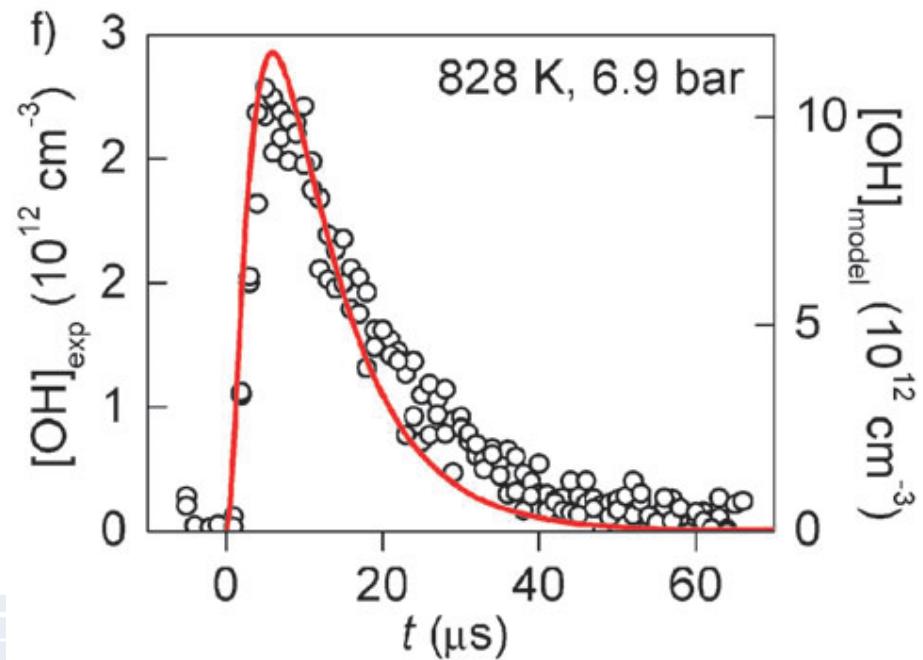
Knepp, Meloni, Jusinski, Taatjes, Cavallotti, Klippenstein,
Phys. Chem. Chem. Phys. 9, 4315 (2007)



Cyclohexyl Oxidation



Sequential



Fernandes, Zador,
Jusinski, Miller, Taatjes,
Phys. Chem. Chem.
Phys. 11, 1320 (2010)

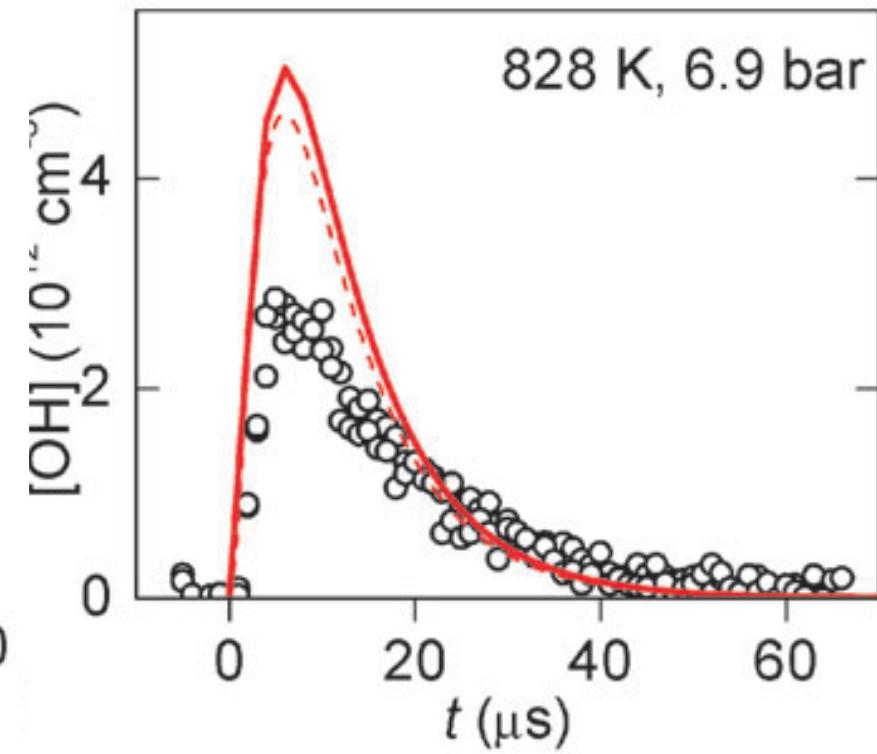
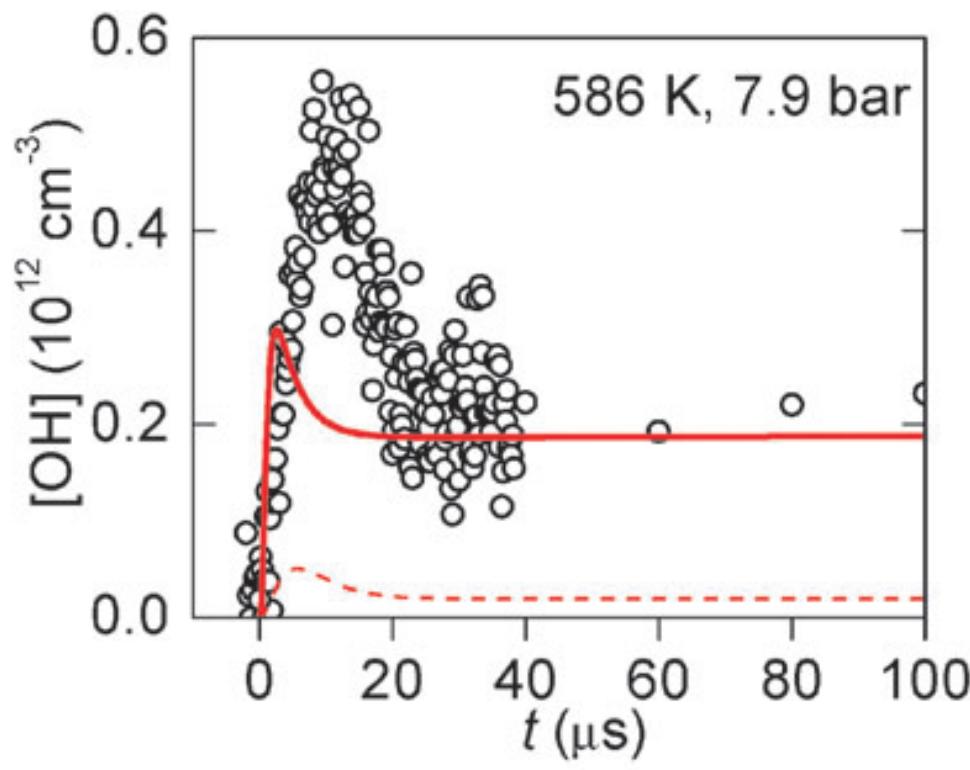


Importance of QOOH + O₂

Add fast chain branching reaction



$$k = 2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$



Summary

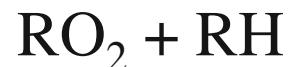
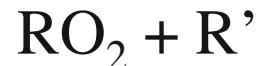
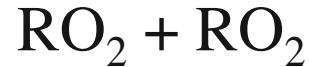
Elementary Rate Coefficients at 100 Bar

Radical Species Profiles – HO₂, HCO at High P

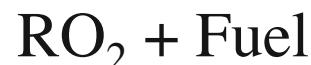
H₂O₂ Kinetics and Species Profiles

Product Branching

RO₂ Kinetics; Especially R = H, CH₃



ROOH Decomposition



Doping

Collisional Efficiencies; Effect of Bath Gas

